Excited States of Wigner Crystals

Fergus Rogers[1] and Pierre-François Loos[1,2]

[1]Research School of Chemistry, Australian National University, Canberra, Australia

[2]Laboratoire de Chimie et Physique Quantiques, UMR5626, Université Paul Sabatier, Toulouse, France

Australian Symposium on Computational Chemistry, UWA, Perth

2nd Dec 2016

The uniform electron gas (UEG) or jellium

A very useful paradigm [Loos & Gill, WIREs Comput Mol Sci 6, 410 (2016)]

- **Definition:**
  "An infinite number of electrons n in an infinite volume V with fixed $\rho = n/V$ embedded in a positive jelly!"
- Central in DFT: cornerstone of the local-density approximation (LDA)
- Good model for metals, not so good for molecules but can be fixed (GGAs, MGGAs, etc)
- Define by **two** parameters:
  1. Electron density ρ or Wigner-Seitz radius r_s
  2. Spin-polarization ζ: paramagnetic $(\zeta = 0)$ vs ferromagnetic $(\zeta = \pm 1)$
- Widely studied but complete understanding elusive

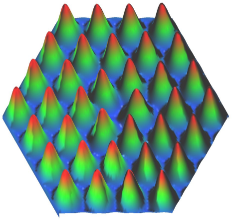
Fluid vs Crystal

Fermi fluid (FF)

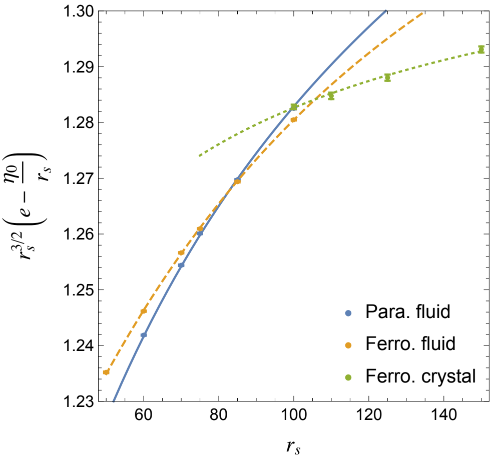
- At high density, the kinetic energy dominates (weakly-correlated regime)
- **Fermi fluid** = delocalized state
- Plane waves are good basis functions!

Wigner crystal (WC)

- At low density, the potential energy dominates (strongly-correlated regime)
- **Wigner crystal** = electrons localize on lattice sites
- Gaussians are a good basis functions!

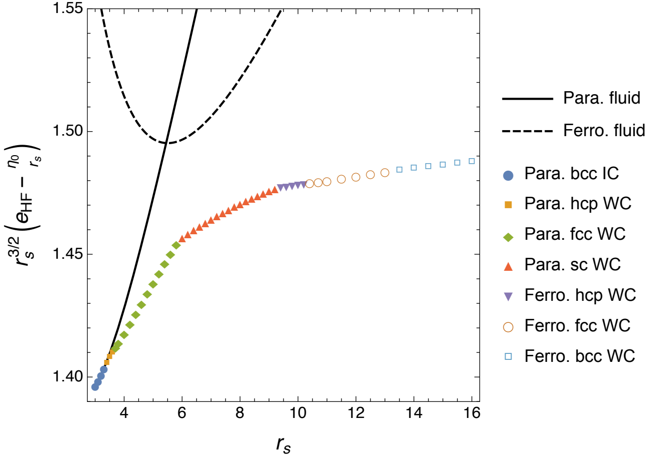


Diffusion Monte Carlo (DMC) ground-state phase diagram (at $T = 0$)



Ceperley & Alder, PRL 45 (1980) 566

Hartree-Fock (HF) ground-state phase diagram



IC = incommensurate crystal

Baguet et al, PRL 111 (2013) 166402

What we would like to study here

Questions to answer

- Why is the HF phase diagram so complicated?
- How symmetry-breaking processes work?
- What about the excited states?

How are we going to answer them?

- Let's stick with the simplest system we can possibly find:
  - One-dimensional electron gas with n electrons
  - Fully-polarized or ferromagnetic (i.e. $\zeta = 1$)
  - Stick with HF (symmetry-broken or UHF calculations)

Rogers & Loos, JCP (submitted) arXiv:1610.09367

Fermi fluid (FF) state

Plane waves and Electron density [Rogers, Ball & Loos, PRB 93 (2016) 235114]

$$\phi_k^{\mathsf{FF}}(x) = \frac{\exp(ikx)}{\sqrt{L}} = \begin{cases} \mathcal{L}_k(x), & k < 0, \\ \mathcal{R}_k(x), & k > 0. \end{cases}$$

$$\boxed{\rho_{\mathsf{FF}}(x) = \sum_{|k| \le k_{\mathsf{F}}} \left| \phi_k^{\mathsf{FF}}(x) \right|^2 = \rho_{\mathsf{FF}}}$$

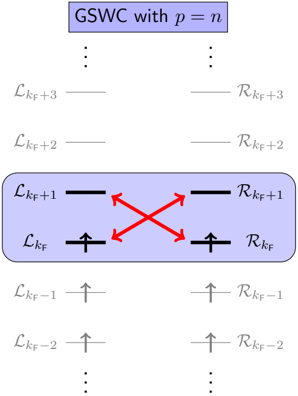
HF energy of the Fermi fluid [Loos & Gill, JCP 138 (2013) 164124]

$$\boxed{e_{\mathsf{FF}}(r_s, n) = t_{\mathsf{FF}}(r_s, n) + v_{\mathsf{FF}}(r_s, n)}$$

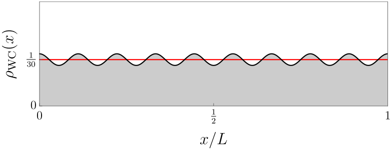
$$t_{\mathsf{FF}}(r_s, n) = \frac{1}{r_s^2} \left(\frac{\pi^2}{24} \frac{n^2 - 1}{n^2} \right)$$

$$v_{\mathsf{FF}}(r_s, n) = \frac{1}{r_s} \left(\frac{1}{2} - \frac{1}{8n^2} \right) \left[\psi\left(n + \frac{1}{2} \right) - \psi\left(\frac{1}{2} \right) \right] - \frac{1}{4}$$

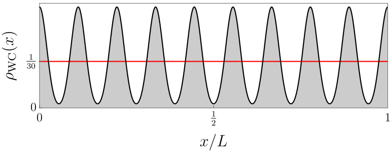
How to grow a ground-state Wigner crystal (GSWC)?



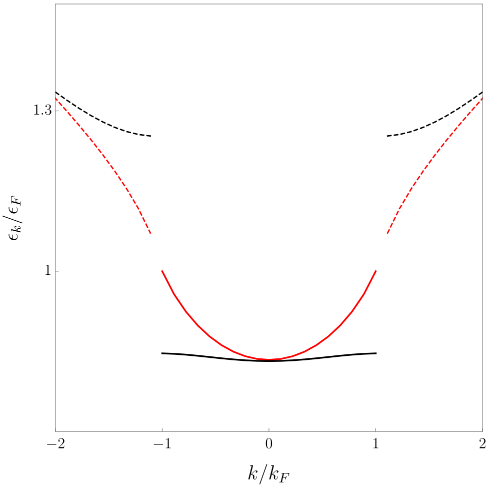
The seed: $\rho_{\text{CDW}}(x) = \rho_{\text{FF}} + A\cos(nx)$



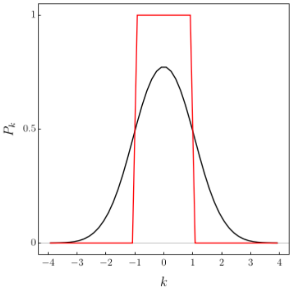
Nucleation ↓ via SCF



MO energies: Fermi fluid vs Wigner crystal

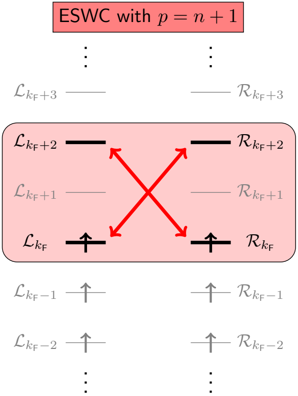


- A gap opens at $\pm k_{\mathrm{F}}$:
  - stabilize occupied MOs
  - destabilize virtual MOs
- **Fermi fluid** = conductor
- **Wigner crystal** = insulator



⇒ **The spatial symmetry is "broken"!**

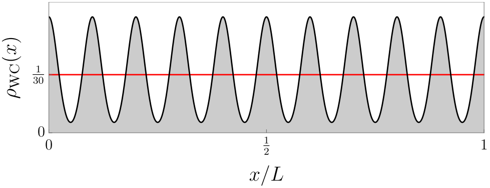
How to grow an unsaturated excited-state Wigner crystal (ESWC)?



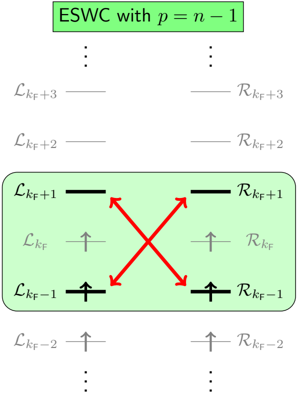
Charge-density wave:

$$\rho_{\text{CDW}}(x) = \rho_{\text{FF}} + A\cos[(n+1)x]$$

Nucleation $\downarrow$ via SCF



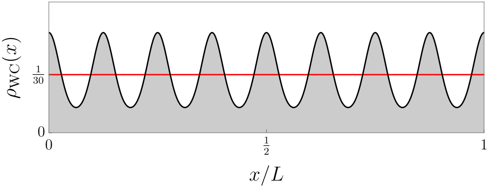
How to grow a supersaturated excited-state Wigner crystal (ESWC)?



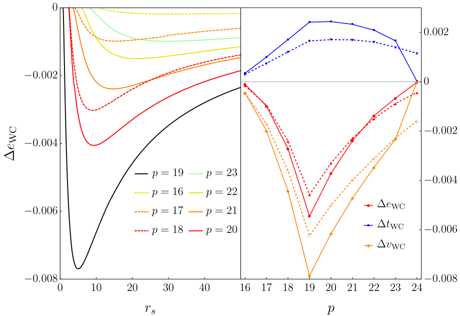
Charge-density wave:

$$\rho_{\text{CDW}}(x) = \rho_{\text{FF}} + A \cos[(n-1)x]$$

Nucleation ↓ via SCF



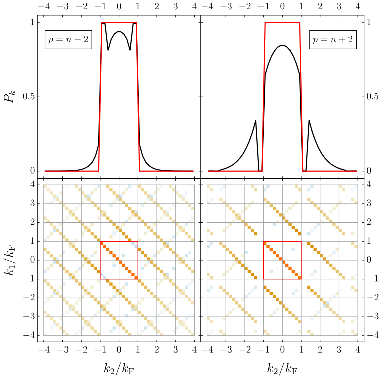
Are they really excited states?



$$\Delta e_{\text{WC}}(r_s, n, p) = e_{\text{WC}}(r_s, n, p) - e_{\text{FF}}(r_s, n)$$
$$\Delta t_{\text{WC}}(r_s, n, p) = t_{\text{WC}}(r_s, n, p) - t_{\text{FF}}(r_s, n)$$
$$\Delta v_{\text{WC}}(r_s, n, p) = v_{\text{WC}}(r_s, n, p) - v_{\text{FF}}(r_s, n)$$

- They are indeed excited states!
- Also true in the thermodynamic limit (i.e. $n \to \infty$)
- All excited-state Wigner crystals are lower in energy than the Fermi fluid!
- Supersaturated and unsaturated crystals cross each other
- Removing peaks $\neq$ adding peaks

Population (top) & Density matrix (bottom)



- Supersaturated excited states (left):

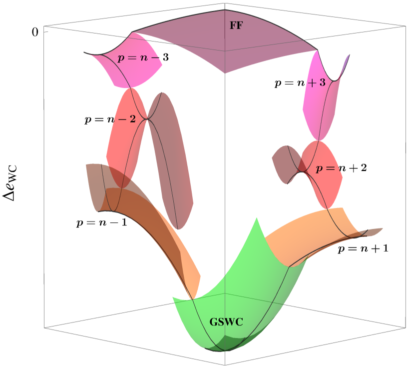
$\Rightarrow$ possess highly-populated PWs with $|k| \leq k_{\text{F}}$

- Unsaturated excited states (right):

$\Rightarrow$ possess sets of vacant PWs with $|k| > k_{\text{F}}$

- Same for harmonics!

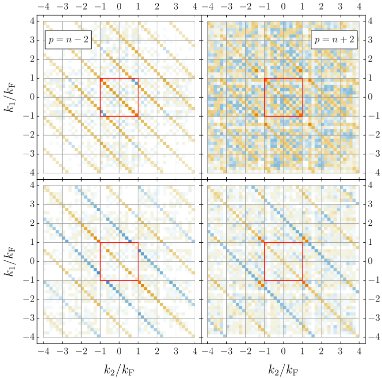
Stability analysis of the HF states



- Ground-state Wigner crystal is a genuine minimum!
- Excited-state Wigner crystals are saddle points of increasing order
- Two disconnected "fountains" of excited states:
  - ⇒ starting at the Fermi fluid
  - ⇒ ending at the ground-state Wigner crystal

Seeger & Pople, JCP 66 (1977) 3045

Detachment (top) and attachment (bottom) matrices



- Supersaturated excited states (left):

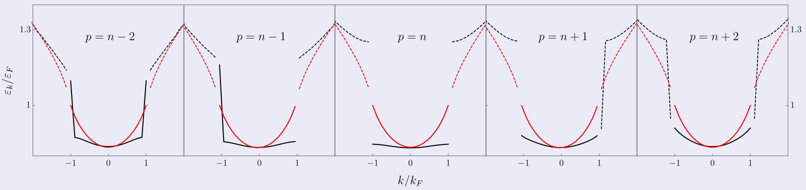
⇒ density jumps from highly-populated PWs $\mathcal{L}_{k_F}$ and $\mathcal{R}_{k_F}$ to PWs with $|k| \gtrsim k_F + 1$

- Unsaturated excited states (right):

⇒ density jumps from PWs with $|k| \lesssim k_F$ to the unpopulated PWs $\mathcal{L}_{k_F+1}$ and $\mathcal{R}_{k_F+1}$

Dreuw & Head-Gordon, Chem Rev 105 (2005) 4009

Peculiarity of MO energies in excited-state Wigner crystals



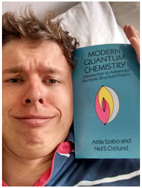
Cool stuff

- For $(n-1)$-peak excited-state Wigner crystal:
  high-energy electron is only conductible in the direction of their initial momentum!

$\Rightarrow$ chiral conductor due to asymmetrical gap!

Students and Funding

- Fergus Rogers (Honours student)



- Research School of Chemistry & Australian National University
- Australian Research Council:
  Discovery Early Career Researcher Award 2013 & Discovery Project 2014

THE AUSTRALIAN NATIONAL UNIVERSITY

Australian Government
Australian Research Council